GEOLOGICAL NOTES

DIFFUSION OF WATER IN SILICATE MELTS[1]

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ABSTRACT

The transport of water in silicate melts is examined from a theoretical point of view, taking into account the presence of both H_2O and OH^- species. It was assumed that only H_2O molecules may diffuse and that a constitutive relationship between the number density n_{H_2O} of H_2O molecules and the total water content (n_Σ) exists such that $n_{H_2O} = g(n_\Sigma)$. This is related to dissociation or to chemical reactions such as H_2O molecular (melt) + Oxygen (melt) $\rightleftarrows$ 2 OH (melt). This approach leads to diffusion transport equations that are intrinsically nonlinear. Three regions are naturally defined: (I) high water content with a normal linear diffusion equation $\partial n_\Sigma/\partial\tau = D\nabla^2 n_\Sigma$, where D is the intrinsic diffusion coefficient of a H_2O molecule in the silicate; (II) an intermediate or transitional region where the transport equation is $\partial n_\Sigma/\partial\tau = D\nabla^2 g(n_\Sigma)$; and (III) a region of low water concentration where the transport equation is $\partial n_\Sigma/\partial\tau = D^*\nabla^2 n_\Sigma^2$. In the latter region, the equation is strongly nonlinear. D^* is a constant diffusion coefficient related to D. It follows that the dissociation of water molecules to form OH^- in silicates automatically implies a nonlinear transport behavior due to the storage of dissociated water molecules in immobile sites. This study of the kinetics of transport will aid in our understanding of speciation and structure in silicate melts.

INTRODUCTION

The purpose of this note is to outline the transport equations for water in silicates taking into account the different mobility of various molecular species. The usual equation for diffusion of a single atomic species is given by $\partial n/\partial\tau = -\vec{\nabla}\cdot\vec{J} = D\nabla^2 n$, where n is the number density of the species, $\vec{J} = -D\vec{\nabla}n$ is the flux of that species, and D the diffusion "constant." If that atomic species is present in different molecular types "i" with their own intrinsic diffusion characteristics, then the total number density of the atomic species is $n_\Sigma = \Sigma_i \alpha_i n_i$ where α_i is a stoichiometric term and n_i the number density of each molecular species. The net flux is $\vec{J}_\Sigma = \Sigma_i \alpha_i \vec{J}_i$. In this case, the diffusion equation becomes $\partial n_\Sigma/\partial\tau = -\vec{\nabla}\cdot\vec{J}_\Sigma$. If only one of the molecular species can diffuse (say $i = 1$), then the equation becomes $\partial n_\Sigma/\partial\tau = -\vec{\nabla}\cdot\vec{J}_1 = \alpha_1 D_1 \nabla^2 n_1$. If there exists a constitutive relationship given by the functional form $n_1 = g(n_\Sigma)$, then the equation, with only one diffusing species, reduces to $\partial n_\Sigma/\partial\tau = \alpha_1 D\nabla^2 g(n_\Sigma)$. It follows that the existence or production of different molecular species of a given element will fundamentally alter the form of the transport equations.

In an early study, a statistical mechanical model of water in silicate systems was presented using entropy considerations in a lattice model which treated the sites of water as H_2O molecules, OH^- molecules breaking oxygen bridges, and in hydrating unshared oxygens associated with cations (Wasserburg 1957). The model was one of weak dissociation of H_2O. For a silicate polymer with r bridging oxygen atoms per unit molecular formula, r is the oxygen index of that silicate (e.g., for $NaAlSi_3O_8$, $r = 8$). In this treatment, the three sites were treated as statistically equally accessible with no energetic differences. The OH sites were considered as paired (that is, Si-OH HO-Si at a given oxygen bridge). From purely geometrical considerations, this model gave the ratio of the number of OH pairs to H_2O molecules as rn_2/n_Σ, where (1) r is the oxygen index of the silicate species and (2) n_2 and n_Σ are the number of "molecules" per cubic centimeter (number densities) of silicate (2) and of total water (Σ) originally included in the conceptual "mixture" of silicate polymer and water. This implies a regular relationship of OH/H_2O as a function of composition with the concen-

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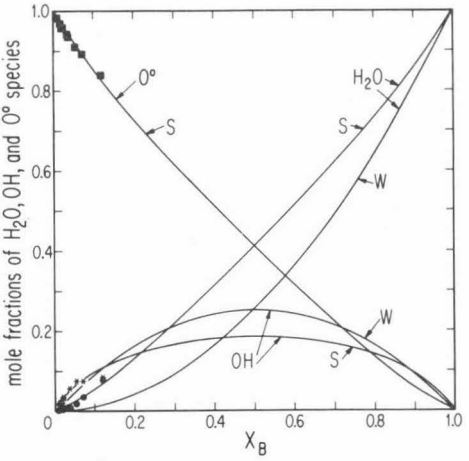

FIG. 1.—The mole fraction of H_2O, OH, and O as a function of $X_B[\equiv n_\Sigma/(n_\Sigma + rn_2)]$. n_Σ is the total number of water molecules per cubic centimeter in the system (H_2O + ½OH); n_2 is the number of silicate "molecules" per cubic centimeter with oxygen index "r." Curves for the mole fraction of OH and H_2O are labeled respectively. The curves labeled S and W are from the models of Stolper (1982) and Wasserburg (1957), respectively. The data are from Stolper (1982). The old model corresponds to the case of $K_1 = 1 - X_B$ (see text).

tration of OH dominating for low concentrations (see fig. 1).

With the advent of modern infrared techniques, it is possible to measure directly the abundance of OH and H_2O. The relationship between SiOH groups and molecularly dissolved H_2O was first found by Moulson and Roberts (1961) and Burns and Roberts (1970) from infrared absorption measurements. In Stolper's (1982*a*, 1982*b*) infrared investigations of H_2O in silicate glasses, it was found that there was a regular relationship of OH and H_2O. He showed that the species were not statistical as assumed by the early model but appeared to be controlled by a reaction between the species of the form:

$$H_2O \text{ (molecular, melt)} + O \text{ (silicate, melt)} = 2OH \text{ (melt)} \quad (1)$$

with an equilibrium constant K_1, where

$$K_1 = (\lambda_{OH})^2/\lambda_O\lambda_{H_2O}. \quad (2)$$

Here, λ_j are the activities of the various water species in the melt and the silicate oxygens (O). This model of local equilibrium between species has been extensively investigated in experimental systems (Silver and Stolper 1985). Stolper's (1982) model implies that the OH bonds are not necessarily paired as was assumed by Wasserburg (1957). The full implications of this model in terms of the structural, energetic, and kinetic implications are not yet clear. For the old model using the ratio of OH pairs to H_2O molecules as rn_2/n_Σ (Wasserburg 1957), we obtain $\lambda_{OH} = X_B(1 - X_B)$, $\lambda_{H_2O} = X_B^2$ and $\lambda_O = 1 - X_B$. Here, $X_B = n_\Sigma/(n_\Sigma + rn_2)$. If we construct the formal relationship on the right hand side of equation 2, we obtain $K_1 = 1 - X_B$. This is close to $K \approx 1$ for the range of concentrations reported by Stolper (1982). The estimates of K_1 by Stolper (1982*b*), based on his experimental data, range from 0.1 to 0.3, which suggest some energetic or structural constraints, as they are distinctly less than one, indicating some restriction of OH sites. A comparison of the mole fraction of H_2O and OH from the dissociative equilibrium of Stolper (1982) and the earlier model of Wasserburg (1957) are shown in figure 1. We note here that use of the parameter X_B to represent the activity of water in the melt, rather than $\lambda_{H_2O} = X_B^2$, leads to an error of a factor of two in the heat of fusion of albite (cf. Wasserburg 1957).

Any discussion of diffusion transport must establish whether the dominant mobile species is OH or H_2O. If an uncoupled distribution of OH existed (that is, not paired as Si-OH HO-Si across pre-existing Si-O-Si bridges), this would suggest that OH might be a mobile species. The effects of dissociation of H_2O in diffusion has been discussed by Doremus (1973) who used the formal solution to the diffusion equation by Wagner (1950) to treat the data of Roberts and Roberts (1964, 1966) and found a good fit. This consideration of dissociation is in the right direction. It fails, however, to provide the proper transport equation and results in an incomplete conceptual view of the overall diffusion process and does not consider wide ranges in concentration. In addition, it yields an error factor of two in the intrinsic diffusion "constant" for asymptotic behavior at low H_2O concentrations.

In an extensive report on the diffusion of H_2O in granitic liquids, Shaw (1974) showed that the (total) solubility of H_2O in obsidian was proportional to the square root of the

H_2O fugacity, indicating a dissociation reaction as outlined above. Shaw (1974) calculated diffusion coefficients by assuming a linear relationship between D and the concentrations of total water. He further showed that the effective isothermal diffusion coefficient in obsidian changed markedly with total water concentration. This was similar to the diffusion effects found in silica glass by Drury and Roberts (1963). Delaney and Karsten (1981), in interpreting H_2O concentration as a function of depth in an ion probe diffusion study, found that the effective diffusion coefficient must be a strong function of concentration. Using a parametric treatment, they inferred that the dependence on concentration was exponential. This suggested functional relationship does not appear to have any theoretical basis. A more recent treatment by Karsten et al. (1982) discusses the problem of H_2O dissociation as a possible cause of the apparently complex behavior. In general, there is growing recognition of the possible significance of H_2O speciation in diffusion in the earth sciences literature, but the interaction between related studies in the ceramics literature has not been large, nor have substantial efforts been made to develop theoretical mechanistic models for diffusion.

It is hoped that this short note may aid in focusing attention on the issue of molecular mechanisms of H_2O and OH transport and the basic equations which govern a simple case. In the following, I will develop a simple diffusion model in which the H_2O molecule is assumed to be the only mobile species and where a local constitutive equation is used to take speciation into account. The resulting model intrinsically exhibits strong concentration dependence.

TRANSPORT MODEL

Let n_Σ be the total number of H_2O molecules and equivalent OH units (H_2O + OH/2) per unit volume. Let us assume that the only mobile species is the H_2O molecule. Take the flux of diffusing water to be $-D\vec{\nabla}n_{H_2O}$, where n_{H_2O} is the number density of H_2O molecules and D is the diffusion coefficient of these species (assumed to be constant). Then, the transport equation is

$$\frac{\partial n_\Sigma}{\partial \tau} = \vec{\nabla} \cdot (D\vec{\nabla} n_{H_2O}) \tag{3}$$

For simplicity, we will first use the old, simplified model by the author, where the fraction of molecules that are H_2O is $n_\Sigma/(n_\Sigma + rn_2)$. As the number density of total water molecules is n_Σ, we obtain

$$n_{H_2O} = n_\Sigma^2/(n_\Sigma + rn_2), \tag{4}$$

Substituting equation 4 into equation 3, the transport equation becomes

$$\frac{\partial n_\Sigma}{\partial \tau} = \vec{\nabla} \cdot D\vec{\nabla}[n_\Sigma^2/(n_\Sigma + rn_2)] \tag{5a}$$

For low water concentrations $n_\Sigma << rn_2$ this reduces to

$$\frac{\partial n_\Sigma}{\partial \tau} \cong \vec{\nabla} \cdot [(2Dn_\Sigma/rn_2)\vec{\nabla} n_\Sigma] \tag{5b}$$

For high water concentrations $n_\Sigma >> rn_2$ this reduces to

$$\frac{\partial n_\Sigma}{\partial \tau} \cong \vec{\nabla} \cdot (D\vec{\nabla} n_\Sigma) \tag{5c}$$

It follows that, at low water concentrations (eq. 5b), the net transport follows a law in which the apparent diffusion coefficient is $2\,Dn_\Sigma/rn_2$ due to the assumed immobility of OH. At zero water concentration, the apparent diffusion coefficient becomes zero. At high concentrations (eq. 5c), where OH is not the dominant species, the equation reduces to the linear case with a constant diffusion coefficient D.

Let us now consider the dissociation reaction (eq. 2). Then

$$K_1 = \lambda_{OH}^2/\lambda_O\lambda_{H_2O} = n_{OH}^2/rn_2 n_{H_2O} \tag{6}$$

where we take n_i to be the number density (see Stolper 1982*b*, eqs. 3.1, 3.2, 3.3, and 4.1). This approach also assumes an effective ideal solution model. For simplicity, we take the number density of silicate oxygens to remain approximately constant, which should be a good approximation for H_2O concentrations below ~10 wt %. The number density of total water molecules n_Σ is given by

$$n_\Sigma = n_{H_2O} + \frac{1}{2} n_{OH}$$

$$= n_{H_2O} + \frac{\sqrt{rn_2K_1}}{2} \sqrt{n_{H_2O}}.$$

The expression for n_{H_2O} as a function of n_Σ is $g(n_\Sigma)$. After some algebra, this becomes

$$n_{H_2O} \equiv g(n_\Sigma) = n_\Sigma + \frac{rn_2K_1}{8} - \frac{rn_2K_1}{8}\sqrt{1 + 16n_\Sigma/rn_2K_1} \quad (7)$$

In equation 7, for the dilute case $16n_\Sigma/K_1rn_2 << 1$, the expression for $g(n_\Sigma)$ may be approximated by $4n_\Sigma^2/rn_2K_1$ if we take the first non-vanishing term in a Taylor expansion. The transport equation (3) then becomes for the dilute case:

$$\frac{\partial n_\Sigma}{\partial \tau} = \vec{\nabla} \cdot [(8Dn_\Sigma/rn_2K_1)\vec{\nabla} n_\Sigma] \quad (8)$$

The apparent diffusion coefficient being $8Dn_\Sigma/rn_2K_1$. The difference between the two solution models at low concentrations is seen in the two scaling terms $2/rn_2$ and $8/rn_2K_1$. For arbitrary concentrations, the transport equation becomes complicated through the dependence of $g(n_\Sigma)$ in equation 7. Inspection of equation 7 shows that, for large concentrations, $n_{H_2O} \approx n_\Sigma$ and the simple linear equation with diffusion coefficient D again results.

Both models of H_2O in silicate melts yield analogous transport equations for low and high concentrations. In general, the profile across a diffusion front may be divided into three regions: high, intermediate, and low H_2O concentrations. The intermediate region is a transition region where the diffusion equation has a complicated form

I	II	III
High H_2O	Intermediate H_2O	Low H_2O
$\frac{\partial n_\Sigma}{\partial \tau} = D\nabla^2 n_\Sigma$	$\frac{\partial n_\Sigma}{\partial \tau} = D\nabla^2 g(n_\Sigma)$	$\frac{\partial n_\Sigma}{\partial \tau} = D^*\nabla^2 n_\Sigma^2$

Here, D^* in region III is a constant related to the intrinsic diffusion coefficient D, as discussed above. Diffusion is relatively rapid in region I, slower in region II, and very slow in region III.

The problem of a diffusion coefficient proportional to the concentration (our region III) has been treated by Wagner (1950) in connection with the diffusion of lead chloride dissolved in solid silver chloride. Wagner (1950) has presented an elegant treatment of this nonlinear problem that is summarized in Crank (1975). Numerical solutions of this equation can readily be obtained. This equation is strongly nonlinear and departs markedly from the usual solution for a constant diffusion coefficient. In particular, there is a strictly defined velocity for the diffusion front.

The analyses presented here show that water diffusion, if governed by transport of the H_2O molecule, should *a priori* yield a distinctive type of behavior which is strongly nonlinear at intermediate and dilute concentrations. This approach appears to describe the existing data on H_2O diffusion at least qualitatively (cf. results by Delaney and Karsten 1981; Karsten et al. 1982, and references therein). It may provide a basis of analyzing the observations in H_2O diffusion experiments and in testing or determining the possible mechanisms of speciation of water in silicate melts. The three distinct regimes of H_2O diffusion may also be related to mechanical properties of hydrated glasses such as hydration rinds and spalling. Substantial increases in volume (i.e., decrease in density) would be expected to be confined to region I and possibly II, with only negligible changes occurring in region III and no effects beyond the diffusion front found by Wagner (1950).

This formal analysis is meant to illustrate the general problem of speciation on the transport problem and to stimulate work in this area. Intensive comparison of theoretical models with well-defined experiments is required in order to achieve any substantial progress. The true mechanisms of speciation and diffusion in silicates have yet to be understood.

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